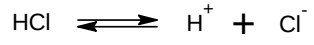
Answer on Question #39252-Chemistry-Organic Chemistry

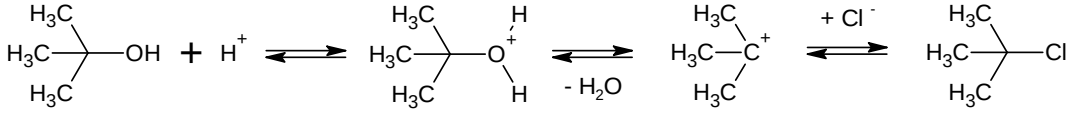
Question

Why only tertiary alcohols undergo halogenation (they are more reactive but what is the reason)?

Answer

Halogenation of alcohols is carried out using the reaction of an alcohol with hydrogen halogenide (usuallu HCl or HBr). The reaction is reversible and occurs *via* intermediate stage of carbocation formation:



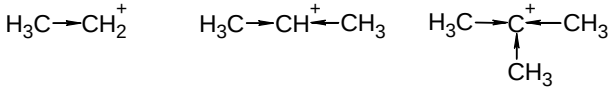


2-methylpropan-2-ol 2-chloro-2-methylpropane

The possibility of the reaction depends on the stability of the carbocation. It must be stable to exist until the interaction with halogen anion. If it is unstable, it readily transforms back to an alcohol.

So, the reason, why tertiary alcohols undergo halogenations (and generally are more reactive in S_N reactions) is that they form more stable carbocations compared to secondary and primary alcohols.

But why tertiary carbocations are more stable? Any alkyl group proves +***I*** effect, pushing electron density to the positively charged carbon atom and, thus, stabilizing it. In primary carbocations only one alkyl group is bound to the positively charged carbon, while in secondary ones two alkyl groups are bound to it and in tertiary carbocations – three. Thus, carbocation stabilization due to the +***I*** effect is three times stronger in tertiary carbocations than in primary ones.



1 +I effect 2 +I effect 3 +I effect

In addition to +***I*** effect, there is also hyperconjugation effect between the electrons of C–H bonds in α-position to the charged carbon. This effect also stabilizes carbocation. There are 2-3 such bonds in primary carbocations, 4-6 – in secondary ones, and 6-9 in tertiary carbocations. This also causes tertiary carbocations to be more stable.